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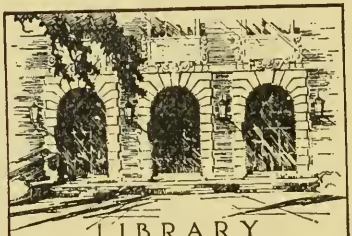

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DEPARTMENT OF CERAMICS

A. V. BLEININGER, Director

A THERMAL STUDY OF BORIC ACID-SILICA MIXTURES

BY

A. V. BLEININGER AND PAUL TEETOR

THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON

BY

R. E. BROWN

1911-1912

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A THERMAL STUDY OF BORIC ACID-SILICA MIXTURES.

By A. V. Bleininger and Paul Teetor, Urbana, Ill.

The subject of possible chemical combinations of silica and boric acid has received some attention in our Transactions,[1,2] and the question raised is interesting inasmuch as such mixtures possess most decidedly the character of glasses or solid solutions. Thermal analysis thus does not promise a fruitful field of investigation. However, of the two methods comprising thermal analysis, the determinations of the softening temperatures is of some interest in itself, since it gives us the general character of the fusion curve of the two components involved.

A thermal lag is not to be expected either in the heating or cooling curves. In the present work, a search was made, however, for such a point based on the statement of Binns, Trans. A. C. S., X, p. 158, in which he records a temperature increase upon the fusion of a mixture of boric acid and silica, due to some exothermal change. The present research deals, (*a*) with the determination of the softening points of SiO_2-B_2O_3 mixtures between the limits B_2O_3-$B_2O_3.3SiO_2$, (*b*) with the determination of heating and cooling curves and (*c*) with an investigation of the solubility of the fused glasses in water. The reagents used were chemically pure hydrous boric acid and silica, the latter being a B. & A. preparation which unfortunately contained several per cent. of sodium chloride and water. In the latter part of the series, fusions were made also with flint which had been passed through a 200 mesh sieve. The calculation of the mixtures was based upon the analyzed silica content, practically 97 per cent. The boric acid was fused, cooled rapidly and kept in a desiccator. It was crushed in a porcelain and pulverized in an agate mortar. Similarly, the silica was ignited and kept in a desiccator. The mixtures were ground together in the agate mortar and fused over the blast lamp in a 10 cc. platinum crucible kept covered during the heating. After some time, the yellow color of the mass disappeared, which seemed to be a measure of the completeness of the fusion. The cooled mass had an opaque

[1] Binns, Trans. A. C. S., Vol. X, p. 158.
[2] Singer, Trans. A. C. S., Vol. X1, p. 676.

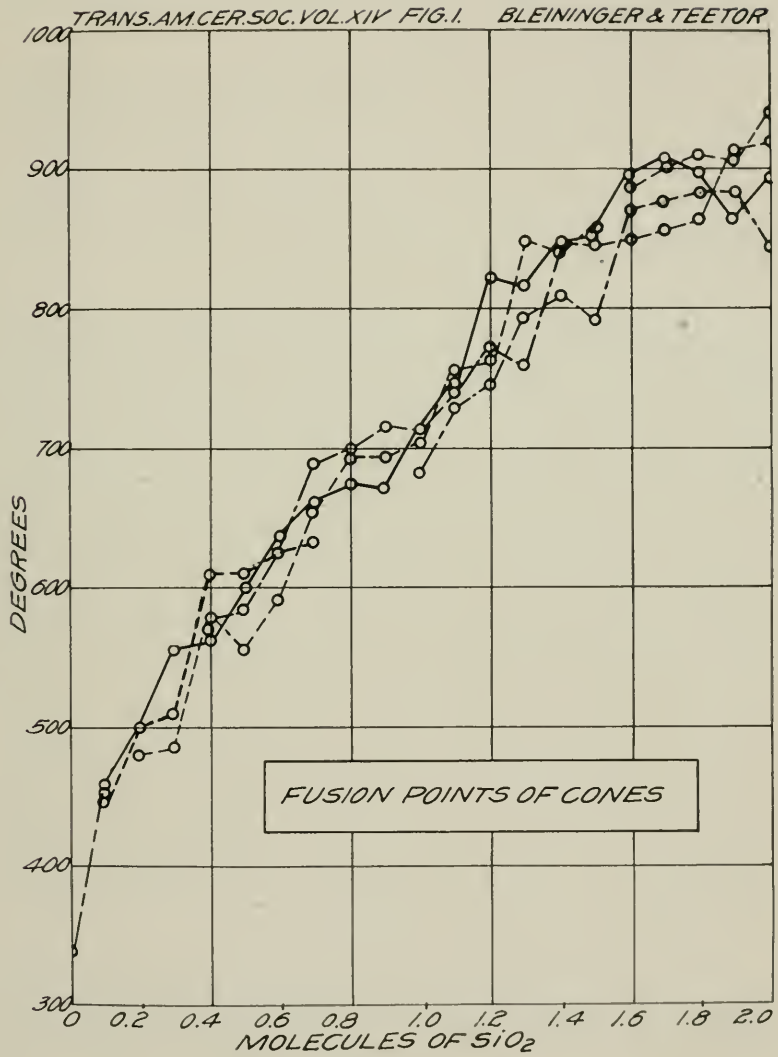
but glassy appearance. The fused mixture was easily removed from the crucible by inserting a platinum rod and quickly cooling in cold water. Then the fusion was pulverized and screened through 80 and 150 mesh screens. The portion passing the 80 but remaining on the 150 mesh screen was used for the solubility samples. This was done in order that no great variations in the surface factor might affect the solubility of the several mixtures.

SOFTENING POINT DETERMINATION.

For this purpose, the fused mixtures of SiO_2 and B_2O_3, ground to a fine powder, were made up with a little water into small cones, and placed in an electric resistance furnace. The specimens were kept in position by means of platinum foil. Since in glasses practically no other criterion is available than the deformation point, the temperature at which the cones bent was taken to represent the softening point. Care was taken to raise the heat at a regular rate by rheostat regulation, and the temperature readings were made by means of a Pt-PtRd thermo-couple, the electromotive force of which was determined by the method of balancing against a standard cell by means of a potentiometer indicator.

Owing to the fact that by mistake water was used in making up the mixtures, some anhydrous boric acid reverted to the hydrous form. This, of course, made it troublesome to determine the deformation point of B_2O_3 owing to the evolution of steam and the resulting bubbling. With the addition of 0.1 SiO_2, the cones seemed to stand up apparently in good shape. The heat given off on adding water to the $B_2O_3.1.5SiO_2$ mixture was so great that the crucible could not be held in the hand. At the same time very little heat was evolved by the $B_2O_3.1.4SiO_2$ and the $B_2O_3.1.6SiO_2$ glasses. On fusing the $B_2O_3.1.5SiO_2$ mixture, it assumed a pink color.

It was soon observed that these glasses were quite viscous. This was illustrated by the fact that a twisted platinum wire on being lowered into the fused mass and again raised was found to draw out a ribbon of glass. It is not surprising, therefore, that the softening points could not be checked, in spite of the fact that the same rate of heating was followed as closely as possible.


TRANS.AM.CER.SOC.VOL.XIV FIG.1. BLEININGER & TEETOR
1000
900
800
700
600
500
400
300
DEGREES
FUSION POINTS OF CONES
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
MOLECULES OF SiO2

In going over this part of the work four times, the results shown in Fig. 1 were obtained. The softening points of the mixtures beyond $B_2O_3.2SiO_2$ are not plotted since the divergence in this part of the series is still greater.

Softening point determinations were also made upon rods drawn from all of the fusions but these likewise gave extremely variable results, considerably lower than those obtained for the cones.

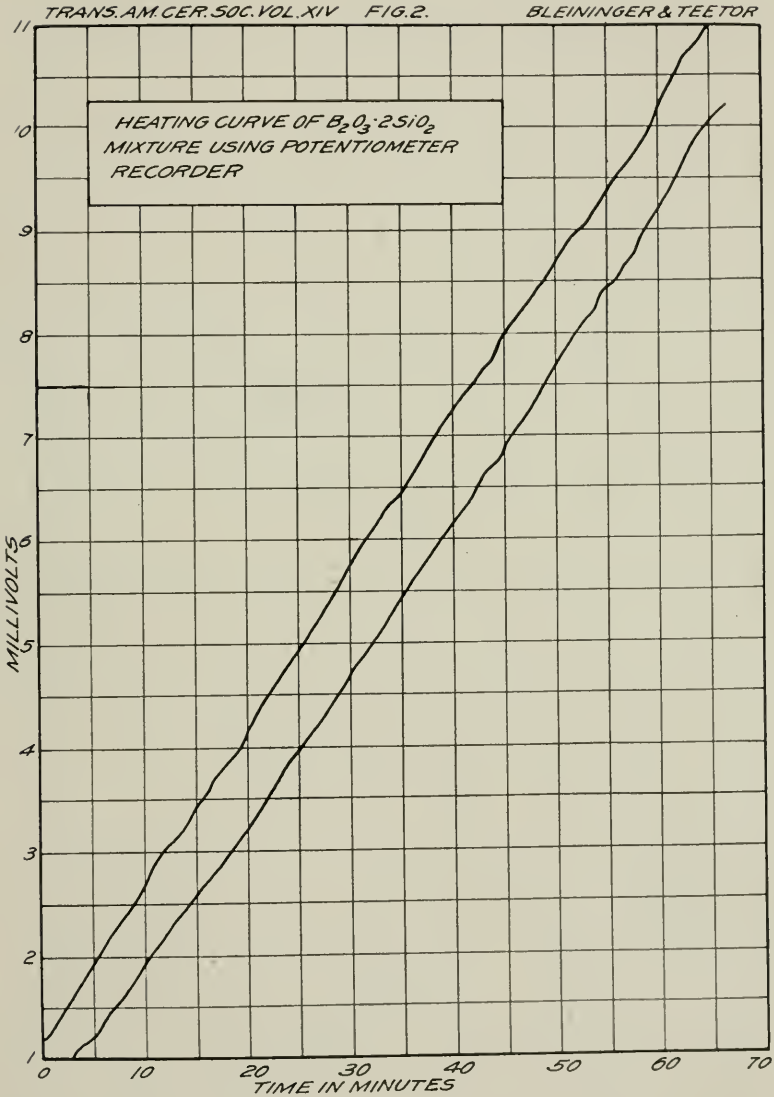
The evidence thus far collected makes it apparent that any reaction taking place under these conditions would be greatly hindered by the internal molecular friction.

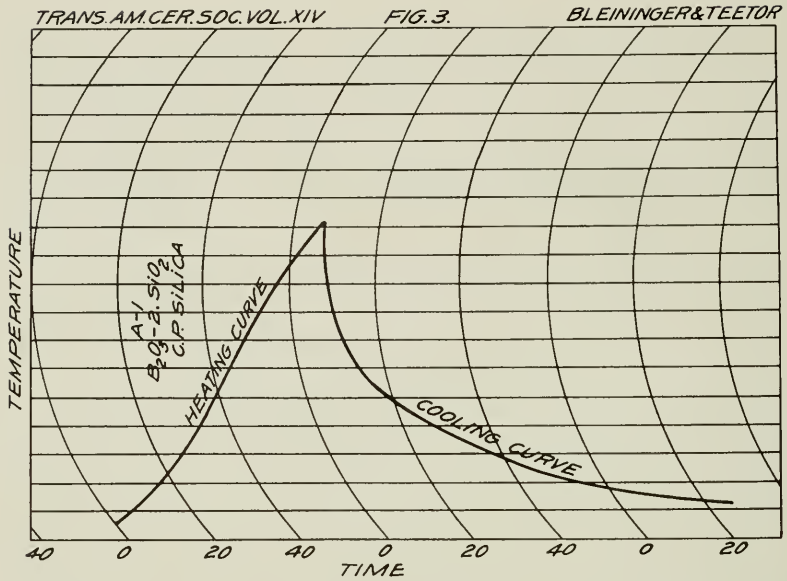
HEATING AND COOLING CURVES.

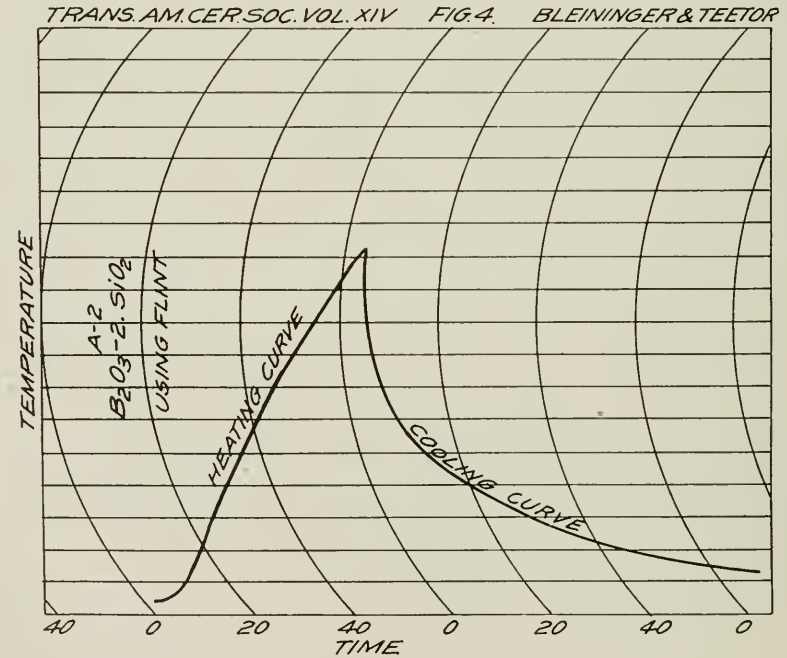
A considerable number of heating and cooling curves were determined with special reference to the $B_2O_3.2SiO_2$ mixture. The latter was prepared from fused B_2O_3 and prepared SiO_2, and from fused boric acid and flint, passed through the 200 mesh sieve. In no instance was there a temperature acceleration or lag observed, and, hence, the observation of Binns was not checked. In Fig. 2, the heating curve in which the couple readings were made by means of a potentiometer indicator is shown. The junction was kept at 0° C. by means of ice. In Figs. 3 and 4, both the heating and cooling curves for prepared silica and flint mixtures as indicated by a Siemens and Halske recorder, making a contact every 16 seconds, are presented. It was observed that on fusing any mixture of B_2O_3 and SiO_2, *without* previous fritting, some vapor was expelled suddenly, carrying evidently a certain amount of boron. This happened also when both the boric acid and silica had been ignited separately to constant weight before mixing. Since Professor Binns used an optical pyrometer, it is quite possible that by focusing upon this vapor the readings were changed as observed by him.

SOLUBILITY DETERMINATIONS.

The different mixtures were fused and pulverized on cooling. The resulting powder was screened through the 80 and 150 mesh sieve. All material coarser than the 80 and finer than the 150 mesh was rejected. One gram samples were then weighed and put in stoppered 250 cc. Erlenmeyer flasks. These were placed

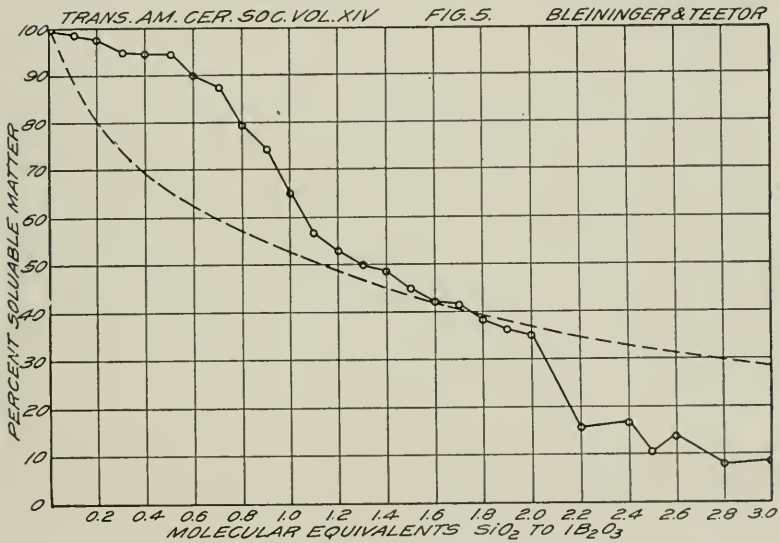

TRANS. AM. CER. SOC. VOL. XIV FIG. 2.
BLEININGER & TEETOR
HEATING CURVE OF $B_2O_3 \cdot 2SiO_2$ MIXTURE USING POTENTIOMETER RECORDER
MILLIVOLTS
TIME IN MINUTES
0
10
20
30
40
50
60
70
1
2
3
4
5
6
7
8
9
10
11


TRANS. AM. CER. SOC. VOL. XIV
FIG. 3.
BLEININGER & TEETOR
TEMPERATURE
A-1
B_2O_3-2. SiO_2
C.P. SILICA
HEATING CURVE
COOLING CURVE
40 0 20 40 0 20 40 0 20
TIME


TRANS. AM. CER. SOC. VOL. XIV
FIG. 4.
BLEININGER & TEETOR
TEMPERATURE
A-2
B_2O_3-2. SiO_2
USING FLINT
HEATING CURVE
COOLING CURVE
40 0 20 40 0 20 40 0
TIME

in a shaking machine together with 200 cc. of distilled water. After shaking for 10 hours and standing over night, the liquid was filtered off and the residue washed. Then 200 cc. of water was again added (including the wash water used) and the flasks were again shaken for one hour. The residue was again filtered and washed. After drying, the residues and paper were ignited and the weights determined. The insoluble matter in each case was brushed off and the paper burnt separately.

The weights of the residues are shown in the curve of Fig. 5.



It is seen that all of the boric acid was dissolved in the first of the series as well as some of the silica. At a point close to $B_2O_3.1.8SiO_2$, however, the solubility curve crosses the line indicating the percentage content of B_2O_3 (shown by the dotted line) which proves that some B_2O_3 has been rendered insoluble. This tendency increases with the silica content. At the molecular ratio 1 : 2 a decided drop occurs indicating the rapid formation of an insoluble glass. As to the cause of this sudden change, we can only conjecture at the present time. To establish the fact that a chemical combination has taken place would require the

running of a parallel series using another criterion such as the specific gravity of the powder. At the present time, however, this evidence might be used to support the claim that we are dealing here with a solid solution representing a chemical union between the silica and the boric acid.

CONCLUSIONS.

Fused boric acid-silica mixtures are typical glasses possessing no definite deformation temperatures.

No thermal phenomena were observed, *i. e.*, there was no absorption or liberation of heat throughout the series B_2O_3 to $B_2O_3.3SiO_2$.

Boric acid when fused with silica first dissolves some of the latter. The amount of matter soluble in water decreases somewhat more rapidly than the B_2O_3 content. Between 2 and 2.2 SiO_2 a decided drop in the solubility of the glasses occurs, indicating that some B_2O_3 has been rendered insoluble. It is quite probable, although not proven, that a chemical combination might take place at this point. The gradual decrease in solubility might thus be ascribed to the formation of some of this combination at an earlier stage. At the point mentioned, a more rapid enrichment would thus take place.

DISCUSSION.

Professor Binns: I am interested in the results secured by Professor Bleininger. When I made the first experiments of this kind I expressly disclaimed any pretension to the ability called for by such work, and I based my chief claim as to the action of boron upon the practical issues as expressed in glaze composition. From this position, which has been confirmed by Dr. Singer and Mr. Stull, I have not had cause to retreat.

[Reprinted from Transactions American Ceramic Society, Vol. XIV, by Permission.]

THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON.[1]

By R. E. Brown, Mt. Savage, Md.

INTRODUCTION.

Classification of Opacifiers.—Opacifiers for the purposes of this work are divided into two classes: (1) partial opacifiers, and (2) absolute opacifiers.

In the first class are included bone ash, fluorite, cryolite, and silica. Bone ash is rarely employed in enamels, but the remaining three, especially the silica, are invariably used. Fluorite and cryolite are advantageous, commercially, both from the standpoint of their low fusibility and their fluorine content. The latter gives them the property of acting as weak opacifiers, thereby decreasing the amount of absolute opacifier needed.[2] The silica, as is shown by the following work, has no opacifying tendencies in itself in this type of glasses but emphasizes and increases the opacity brought about by certain opacifiers proper.

In the second class, the opacifiers, *per se*, are arsenious oxide, zirconium oxide, tin oxide and antimony oxide. Arsenious oxide finds a very limited use, being employed only for decorative work on jewelry and art ware. Zirconium oxide is not widely used; while some consider it too expensive for commercial work, others regard it a cheap opacifier as a substitute for tin oxide.[3] Tin oxide is by far the most widely used of the opacifiers, and is employed not only in the enameling of sheet iron and cast iron, but in the enameling of clay products as well.

Antimony oxide has had, to date, only an extremely limited use as an opacifier. It has been used to some extent in Germany in conjunction with zinc oxide as a substitute for tin oxide.[4] It has been used in this country to some extent, and in one case its use in conjunction with other ingredients is patented as "a substitute for tin oxide."[5] In a "Note on White Antimony

[1] Abstract of a thesis fulfilling part of the requirements for the degree of Bachelor of Science in Ceramics, University of Illinois.

[2] Mayer and Havas, Sprechsaal, XLII, 460–461.

[3] La Ceramique, 11, 100–101. Keram Rundschau, XVI, 89–91, 135–139.

[4] Ph. Eyer, Stahl und Eisen, XVIII, 1097, 1099.

[5] U. S. Patent, 932,839.

Enamels," Bock points out the dangers of the use of antimony oxide in enamels for cooking vessels, but no mention is made of its employment in enamels for cast iron.[6]

The most expensive constituent of the ordinary commercial enamel is the opacifying agent, tin oxide, both by reason of the high market price and the quantity employed. The prices of antimony oxide and tin oxide in barrel lots are at present $10^1/_2$ and 45 cents per pound, respectively.

Object of Work.—It was with a view to using the cheaper opacifier for cast iron enamels that this work was undertaken. The work attempts to determine, in a practical way, the conditions under which antimony oxide may be used in enamels.

EXECUTION OF WORK.

Preparation of the Enamels.—In carrying out a series the ingredients of the two extremes of a series were weighed up and mixed thoroughly by passing 5 or 6 times through a 20 mesh screen. The batch was next put into a small fire clay crucible (capacity about 250 grams of the raw batch) and fritted in a pot furnace, fired by a blast lamp using artificial gas and compressed air as fuel. After melting and becoming relatively free from bubbles the contents were poured into water. It was then dried, again put into the crucibles and refritted, care being taken in this second fritting to prolong the heating to such length of time that no bubbles were given off. As soon as bubbles had ceased to form, the contents were again quenched by pouring into water. The shattered glass was dried and then ground in 8 inch, porcelain, ball mills so as to pass a 200 mesh sieve.

The two extremes of a series, now in a powdered form, were weighed out in the proper proportions to form the intermediate enamels. These were now mixed by rubbing 5 or 6 times through a 60 mesh sieve.

The Ingredients.—The raw ingredients employed in introducing the following constituents with the molecular weights used were as follows:

ZnO: Introduced as zinc oxide (81).

PbO: Brought in as red lead Pb_3O_4 (685).

[6] Chem. Ztg., XXXII, 516–517.

BaO: Where employed, was brought in by barium carbonate (197).

CaO: Brought in by fluorite (78), whiting (100), and hydrated lime (74).

Na_2O: Introduced as sodium carbonate (106), borax (382), and cryolite (210).

K_2O: Brought in by potassium nitrate (101) and potash feldspar (557).

MgO: Brought in by magnesium carbonate (84) and magnesium oxide (40).

Al_2O_3: Potash spar (557) was used as the main source of alumina. Small amounts of cryolite, Na_3AlF_6 (210) were also used.

B_2O_3: This was brought in by using borax (382) in the cover enamels and as borax and boric acid (62) in the ground coats.

SnO_2: Brought in as tin oxide (150).

Sb_2O_3: Introduced as white oxide of antimony (288).

SiO_2: Brought in as potash feldspar (557), and as flint (60).

In addition to the above ingredients, ammonium carbonate was used in some of the enamels of the later series. This volatilizes readily and serves as a clarifier of bubbles in the glass during fritting.

Trial Pieces.—The trial pieces were small circular discs $^1/_8$″ thick and 2″ in diameter with a raised center. The iron used for casting these trials did not prove to be of a very satisfactory grade as it frequently produced large bubbles or blisters in the enamels, probably due to the sulphur content of the iron.

The trials were cleaned by pickling for 20–30 minutes in a dilute solution of hydrochloric acid so as to remove the scale and any oxide present. After this they were washed and scrubbed and then dipped in a dilute solution of sodium carbonate so as to neutralize all of the acid. They were then scrubbed and washed again, the surface water was wiped off, and the trials were put into a warm oven. Even with this seemingly thorough treatment, the coat of carbon (left by dissolving the iron) was not entirely removed, and hence gave rise to bubbles during the burning process. Another method of cleaning the iron, used in the latter part of the work, proved very effective. In this, the iron

was pickled as before and then put into a ball mill with sand and water; thus all of the carbon was effectually removed with the result that less trouble as regards bubbling was experienced.

The ground coat was applied to the trials by dipping, care being taken to secure a thin coat that was as uniform as possible.

Composition of the Ground Coat.—The ground coat chosen was of the composition shown:

$$\left.\begin{array}{l} 0.30\ K_2O \\ 0.24\ Na_2O \\ 0.159\ CaO \\ 0.219\ MgO \\ 0.081\ PbO \end{array}\right\} \left.\begin{array}{l} 0.297\ Al_2O_3 \\ \\ 0.31\ B_2O_3 \end{array}\right\} 2.19\ SiO_2$$

Batch weights: 15 flint; 30 potash feldspar; 10 boric acid; 5 KNO_3; 5 Pb_3O_4; 2.2 $Ca(OH)_2$; 2.3 MgO; 10.0 cryolite; 1.0 fluorite.

The trial piece, after being slush coated and dried, was placed in the furnace, which had been heated to the temperature of burning. As soon as the iron had attained a sufficient heat for fusing the ground enamel, it appears to "melt" not unlike a coat of frost or snow. This commences at one spot and soon has extended over the whole trial. The trial now has a glossy appearance. Almost coincident with this, innumerable bubbles are formed which "break" at once. This continues for a short time, after which the glossy coating or glass smooths down. It is at this point, in the writer's judgment, that the burning of the ground coat is complete. If the trial is not removed at once, larger bubbles are formed, but the glass is then decidedly more viscous than when the preliminary bubbles were formed. When they break, if they break at all, they leave a rough slag on the surface of the trial as is shown by cooling the trial piece.

Burning the Enamels.—The furnace used for the enameling was of the open-fired type, *i. e.*, without a muffle chamber, and was fired by the use of artificial gas and compressed air as fuel. Although this is not the type of furnace best suited for this kind of work, it was the only one available and there was no time for the construction of a more suitable one. The temperature of burning was measured by a Le Chatelier pyrometer, the couple of which was inserted so that its junction point was at the side

of the trial. The holder for the trial piece consisted of a bar of iron "upset" at one end and so shaped as to fit on the inside of the trial piece.

Series I.

REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN A TIN ENAMEL.

This series was carried out by replacing the tin oxide in an enamel similar to that given by Riddle in his "Types of Enamels for Enameling Cast Iron Sanitary Ware," Trans. A. C. S., Vol. IX, with antimony oxide, thus:

0.25 Na_2O		
0.10 MgO		
0.15 PbO	0.15 Al_2O_3	1.00 SiO_2
0.15 BaO		
0.15 K_2O	0.20 B_2O_3	0.15 SnO_2–0.075 Sb_2O_3
0.05 ZnO		
0.15 CaO		

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	$BaCO_3$	CaF_2	ZnO	$MgCO_3$	Borax	K. Spar	Flint	SnO_2	Sb_2O_3
1	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.15	0.00
2	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.1125	0.0188
3	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.075	0.0375
4	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.0375	0.056
5	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.00	0.075

Description of Trials.—No. 1 is a good enamel and is a typical tin enamel. All of the rest of the series, with the possible exception of No. 2, are very poor. A peculiar "puckery" or matte texture exists, the surface is rough and uneven, and the enamel flies off in patches, resembling shivering of clay ware. In the trials of enamels 3 and 4, the "puckery" effect is partially overcome by raising the burning temperature. The shivering is also lessened by this treatment. It is also evident in this series as well as in the rest of the work that where an enamel is applied, too thick shivering is more likely to occur.

Thinking perhaps that the "puckery" effect might be overcome partially by making a more easily fusible enamel it was

decided to run a series with a more fusible RO combination. It was also suggested that the "puckery" effect might be due to the barium which reacted with the sulphur present in the Sb_2O_3.[7] Some of the Sb_2O_3 was tested and found to contain sulphur.

A series embodying the two above ideas was accordingly carried out as given below. Although it was not conducted strictly on a scientific basis it is sufficient to show in a practical way the desired effect.

Series II.

VARIATION OF BARIUM OXIDE AND ITS EFFECT ON ANTIMONY OXIDE.

0.25–0.54 Na_2O		
0.10–0.00 MgO		
0.15–0.15 PbO	0.15–0.16 Al_2O_3	1.00 SiO_2
0.15–0.16 K_2O		
0.05–0.05 ZnO	0.20 B_2O_3	0.075 Sb_2O_3
0.15–0.10 CaO		
0.15–0.00 BaO		

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	$BaCO_3$	CaF_2	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	$MgCO_3$	Spar	Flint	Sb_2O_3
1.....	0.15	0.05	0.15	0.15	0.05	0.00	0.00	0.00	0.10	0.10	0.15	0.10	0.075
2.....	0.21	0.05	0.10	0.10	0.05	0.02	0.02	0.03	0.10	0.07	0.148	0.14	0.075
3.....	0.29	0.05	0.05	0.05	0.05	0.04	0.04	0.07	0.10	0.03	0.136	0.18	0.075
4.....	0.35	0.05	0.00	0.00	0.05	0.06	0.06	0.10	0.10	0.00	0.13	0.22	0.075

Description of Trials.—The "puckery" effect has decreased toward the end of the series which contains no barium and in No. 4 is not present at all. This enamel is a fair enamel which adheres well. No. 1 is somewhat shivered. This series shows from a practical standpoint that barium should not be used to any very large extent in an enamel where there is a contact with sulphur gases. Its use, however, in enamels where tin is used as an opacifier is very much desired, owing to its ability to decrease shivering.

[7] Sb_2O_3 is prepared from stibnite, Sb_2S_3, by roasting in air, hence sulphates are formed which, if not entirely removed, would combine with the barium compounds.

Series III.

VARIATION OF THE SILICA CONTENT.

This series was varied between the limits of 1.00 and 2.00 equivalents of silica as shown:

$$\left.\begin{array}{l} 0.10\ CaO \\ 0.54\ Na_2O \\ 0.15\ PbO \\ 0.16\ K_2O \\ 0.05\ ZnO \end{array}\right\} \left\{\begin{array}{l} 0.16\ Al_2O_3 \\ 0.20\ B_2O_3 \end{array}\right\} \left\{\begin{array}{l} 1.00\text{–}2.00\ SiO_2 \\ 0.075\ Sb_2O_3 \end{array}\right.$$

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.22	0.075
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.345	0.075
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.47	0.075
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.595	0.075
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.72	0.075
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.845	0.075
7.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.97	0.075
8.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.095	0.075
9.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.075

Description of Trials.—Nos. 1, 2 and 3 have an egg shell-like texture but otherwise are fair enamels. The trials of enamels Nos. 4 and 5 are better and do not show the above texture to such a degree. No. 6 is a fair enamel but is a trifle dull. No. 7 is a good enamel and adheres well. It is whiter and has a better gloss than the average commercial enamel. Enamel No. 8 is whiter than No. 7 and has a better gloss. A few of the trials shiver somewhat, showing that the silica is a trifle too high. Enamel No. 9 has shivered still more, but on the trials where it held, it is the whitest and most brilliant of the series. Enamels Nos. 8 and 9 have an exceptionally white color and are more than the equal of the average tin enamel in this respect.

The result of this series seems to show that the last two enamels are too high in silica and also that a silica content of over 1.85 equivalents is conducive in shivering. The burning temperature rises as the silica content increases; but this heat,

even with the enamels containing 2.0 SiO_2, did not cause the iron to deteriorate to any visible extent. As silica increases, the whiteness is increased, and it is evident that a sacrifice must be made of part of the whiteness in order to obtain enamels that do not shiver.

Series IV.

VARIATION OF ALUMINA.

This series was run between the limits of 0.1 and 0.2 equivalent of Al_2O_3. To bring in the Al_2O_3 in combined form, *i. e.*, as spar, it was necessary to change the RO with respect to K_2O and Na_2O thus:

0.16–0.20 K_2O		
0.15 PbO	0.10–0.20 Al_2O_3	1.80 SiO_2
0.10 CaO		
0.54–0.50 Na_2O	0.20 B_2O_3	0.075 Sb_2O_3
0.05 ZnO		

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	K_2CO_3	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1....	0.35	0.05	0.05	0.06	0.06	0.06	0.10	0.10	0.07	1.38	0.075
2....	0.342	0.05	0.05	0.049	0.06	0.06	0.10	0.10	0.09	1.26	0.075
3....	0.334	0.05	0.05	0.038	0.06	0.06	0.10	0.10	0.11	1.14	0.075
4....	0.326	0.05	0.05	0.025	0.06	0.06	0.10	0.10	0.13	1.02	0.075
5....	0.318	0.05	0.05	0.013	0.06	0.06	0.10	0.10	0.15	0.90	0.075
6....	0.31	0.05	0.05	0.00	0.06	0.06	0.10	0.10	0.17	0.78	0.075

Description of Trials.—All enamels of the series are good enamels with whiteness increasing toward No. 6, *i. e.*, with increase of Al_2O_3. The temperature required for maturing increases, however, with the Al_2O_3. The best enamel of the series, taking burning temperature, whiteness, gloss, and adhesive properties into consideration, is No. 4 containing 0.16 Al_2O_3.

Series V.

VARIATION OF ANTIMONY OXIDE.

This series as well as the remaining two series was carried out in two parts, A and B, the two parts being practically alike

except for the silica content. Part B was carried out first and the limits of Sb_2O_3 were not high enough, hence these were changed in A.

Series V, A.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\ \left\{\begin{matrix}0.16\ Al_2O_3\\0.20\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.8\ SiO_2\\0\text{–}0.14\ Sb_2O_3\end{matrix}\right.$$

Series V, B.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\ \left\{\begin{matrix}0.16\ Al_2O_3\\0.20\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}2.0\ SiO_2\\0\text{–}0.11\ Sb_2O_3\end{matrix}\right.$$

V, A. Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.00
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.02
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.04
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.06
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.08
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.10
7.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.12
8.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.14

V, B. Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.00
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.022
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.044
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.066
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.088
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.11

Description of Trials.—The trials of enamel 1 A have but

slight opacity. No. 2 A has a trifle more and so on up the series, Enamel No. 3 A has a fair opacity, No. 4 A and 5 A are good enamels, No. 5 A being the whitest. No. 6 A is a good enamel. It is whiter than No. 5 but is not quite so glossy. No. 7 is a good enamel and is a trifle "matte" in texture. No. 8 has a beautiful matte texture and differs from all the rest of the series in this respect. One of the trials, however, shows a tendency to shiver but this may possibly be due to the mode of application. Enamel No. 5 is the best of the A part of the series, taking gloss, finish, and general appearance into consideration, while for a dull or matte texture No. 8 is the best. Enamels No. 7 and 8 require a higher temperature for burning, thus indicating that high antimony decreases the fusibility.

With part B of the series shivering is more evident in every case. The enamels which held are, however, of greater brilliancy and opacity, enamel No. 2 of A being identical in appearance with No. 1 of B. Enamels 2, 3 and 4 of part B are practically the same as 3, 4 and 5 of part A respectively. From this we would conclude that 0.016 equivalent of Sb_2O_3, in this range of silica content, has about the same opacifying effect as 0.02 equivalent of silica.

Series VI.

REPLACEMENT OF ANTIMONY OXIDE BY TIN OXIDE IN AN ANTIMONY ENAMEL.

This series, also using two different equivalents of silica, was carried out as follows:

VI, A.

0.16 K_2O		
0.05 ZnO	0.16 Al_2O_3	1.80 SiO_2
0.10 CaO		
0.15 PbO	0.20 B_2O_3	0.075 Sb_2O_3–0.15 SnO_2
0.54 Na_2O		

VI, B.

0.16 K_2O		
0.05 ZnO	0.16 Al_2O_3	2.0 SiO_2
0.10 CaO		
0.15 PbO	0.20 B_2O_3	0.075 Sb_2O_3–0.15 SnO_2
0.54 Na_2O		

Batch formulae (in equivalents).

VI, A.

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3	SnO_2
1....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075	0.00
2....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.056	0.038
3....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.038	0.075
4....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.019	0.1125
5....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.00	0.15

VI, B.

1....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075	0.00
2....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.056	0.038
3....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.038	0.075
4....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.019	0.1125
5....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.00	0.15

Description of Trials.—All enamels of the A part of the series adhere tenaciously and are good enamels. Enamel No. 1 has more opacity and whiteness than No. 5, these two properties decreasing uniformly between these extremes. The antimony enamel requires a slightly higher temperature for maturing, but not to such extent as to be detrimental to the iron.

In the B part of the series shivering is much in evidence, due to the increased silica. Enamels Nos. 1 and 2 have good opacity but Nos. 3 and 4 are much inferior in this respect. In enamel No. 5 the silica has dissolved the SnO_2 almost entirely. Taking the results of this series we would conclude that SiO_2 at the higher limit is opposite in effect with regard to Sb_2O_3 and SnO_2. In the case of Sb_2O_3 the opacity, whiteness and brilliancy are increased, while with SnO_2 these properties, notably the opacity, are decreased. Shivering, however, is increased in either case. The results obtained in part A of the series are not in accord with those of Riddle whose high limit of silica was 1.25 equivalents. In enamel No. 5 part A as given above, a good white enamel was obtained using 1.8 equivalents of silica.

It might be interesting to note also at this point, the behavior of the enamels on wrought iron. The enamels of part A were applied to iron washers, and although they had not been

previously cleaned, the enamels held perfectly and were of good whiteness, brilliancy and texture.

Series VII.

VARIATION OF BORIC OXIDE.

This series employs two equivalents of silica and the Na_2CO_3 content is varied in order to reach the lower limit of B_2O_3 still maintaining the same ratio.

VII, A.

0.16 K_2O 0.05 ZnO 0.10 CaO 0.15 PbO 0.54 Na_2O	0.16 Al_2O_3 0.10–0.40 B_2O_3	1.80 SiO_2 0.075 Sb_2O_3

VII, B.

0.16 K_2O 0.05 ZnO 0.10 CaO 0.15 PbO 0.54 Na_2O	0.16 Al_2O_3 0.10–0.40 B_2O_3	2.00 SiO_2 0.075 Sb_2O_3

VII, A.

Batch formulae (in equivalents)

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.02	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.02	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.02	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.02	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.02	0.075
7.....	0.25	0.05	0.05	0.03	0.06	0.10	0.2	0.13	1.02	0.075

VII, B.

1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.22	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.22	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.22	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.22	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.22	0.075
7.....	0.250	0.05	0.05	0.03	0.06	0.10	0.200	0.13	1.22	0.075

Description of Trials.—All enamels of part A adhere well and are good white enamels up to No. 6. Nos. 6 and 7 have a yellowish cast and are not all desirable enamels. Bubbling is also evident in the enamels of higher B_2O_3 content. Enamel No. 1 is the whitest of the five enamels.

The results obtained in part B are substantially the same as those of part A. The enamels are whiter, however, than the ones of the same B_2O_3 content and the yellowish cast of enamels 6 and 7 of part A has disappeared in the corresponding enamels of part B. Shivering is present to quite a large extent in part B, due to the high silica. As in part A, bubbling is prominent in the enamels of the higher B_2O_3 content. The difference in whiteness of the high and low B_2O_3 enamels in part A is not so pronounced in this part of the series. Enamels B 1 and B 7 have very little difference in whiteness, B 1 being a little the whitest. The difference in maturing temperature is however quite large and the tendency to bubbling is more evident.

The results indicate that the lower the B_2O_3 the better and whiter are the enamels. The limits for desirable enamels are about 0.15–0.30 B_2O_3.

LIMITS OF THE INGREDIENTS.

The limits of the ingredients and their effects established by this work are as follows:

SiO_2: The effect of silica is to increase brilliancy, whiteness, acid-resisting properties and gloss. If increased too high, shivering takes place and the maturing temperature is too high. The limits are about 1.65–1.85 equivalents, those nearer the higher limit being the preferable.

Al_2O_3: Increased Al_2O_3 increases the temperature for maturing and gives whiter enamels. The high limit is around 0.18 equivalent. The low limit was not established but for commercial enamels is probably about 0.13 equivalent.

Sb_2O_3: The effect of Sb_2O_3 is to increase the maturing temperature, and to increase the whiteness and opacity when employed between the limits of 0.0–0.09 equivalent Sb_2O_3. If used between the limits of 0.1–0.14 equivalent the enamels are dull at the lower limits and matteness increases at the higher.

At the high limit, 0.14 equivalent, shivering is likely to occur.

For brilliant enamels of good opacity and texture the limits are 0.06–0.09 equivalent, about 0.075 being preferable.

SnO_2: No variation of the SnO_2 content was made but a good enamel was obtained using 0.15 equivalent of SnO_2.

B_2O_3: The effect of increased B_2O_3 is to lower the maturing temperature, to increase the tendency to produce bubbles, to decrease the whiteness when used above a certain limit, increase gloss, and to increase the solubility of the enamel. The limits are about 0.15–0.3 equivalent, those nearer the lower limit being preferable.

BaO: The effect of BaO in Sb_2O_3 enamels is to produce a "puckery" or matte effect. This is no doubt due to the sulphur arising from the Sb_2O_3 and the fuel gases, which comes in contact with the barium compounds.

The most likely enamel taking all points into consideration is:

$$\left.\begin{matrix} 0.16\ K_2O \\ 0.05\ ZnO \\ 0.10\ CaO \end{matrix}\right\} 0.16\ Al_2O_3 \quad 1.80\ SiO_2$$

$$\left.\begin{matrix} 0.15\ PbO \\ 0.54\ Na_2O \end{matrix}\right\} 0.20\ B_2O_3 \quad \Big\} 0.075\ Sb_2O_3$$

DISCUSSION.

Professor Staley: Why do you not include the fluorine in your formula? No one will be able to calculate the batch from the formula unless you do so. Moreover, it makes a vast difference whether an enamel contains a small or a large amount of this element.

Mr. Brown: I do not think it is necessary. I introduced it as cryolite, using 0.06 equivalent of cryolite throughout.

Professor Staley: Mr. Brown, I just want to ask one more question. Did you get an absolutely pure white enamel, or was it of a greenish or bluish tint? There have been many attempts made to use antimony in place of tin oxide in cast iron enamels, but it has never given a satisfactory white. They get a tint they call white, but it is not a commercial white. Do you have any idea of how to avoid getting that greenish, bluish white so characteristic of antimony oxide?

Mr. Brown: I did not carry on work to eliminate the cast you speak of. The cast was not present to an aggravated extent that I could see. A number of others said the same thing. There is a slight bluish cast or tint in some of the trials.

Professor Staley: In your final enamel as well as in all the others?

Mr. Brown: It was not so pronounced in this case, but more so in the enamels of higher silica content.

Mr. Burt: I noticed in speaking of the enameled iron industry they always speak of dusting the enamel on and I would like to get a little description of what the mechanical process is—of what is involved in this dusting on of the glaze.

Professor Staley: In a paper ("The Manufacture of Enameled Iron Sanitary Ware," Trans. A. C. S., Vol. VIII, p. 172) I published several years ago, you can find a description of the ordinary method of making a piece of enameled cast iron. The only difference between the method described there and the method used at present is the use of a mechanical agitator.

Mr. Burt: What mesh sieve do you use?

Professor Staley: The sieve is a fifty- or sixty-mesh sieve.

Mr. Brown: I would like to ask Professor Staley what his opinion is of the fluorine in a fused enamel—whether it is volatilized or whether it is retained in the enamel. I have read of several instances where they analyzed for fluorine and found it in the enamels in small quantities.

Professor Staley: That is all a matter, in my mind, of how hard, how long, and how hot you heat the enamel. You can volatilize it all, or you can have the larger portion of it stay in. If it is all volatilized you have no opacifying effect from the use of fluorides. In cast iron enamels that are heated or fritted in the ordinary length of time, the large bulk of fluorine stays in.

NOTE PREPARED AFTER READING THE PAPER.

Professor Bleininger: It seems to me that Mr. Brown has solved his problem satisfactorily. He has accomplished two things, *viz.*, the production of a white enamel which compares favorably with the best tin enamels, in the opinion of impartial observers, and he likewise has shown clearly the kind of enamel

required for the use of antimony as an opacifier, which differs somewhat from the common type.

As regards the poisonous quality of antimony compounds, Rickmann, Sprechsaal, XLV, 115–117, says that during an experience of ten years the use of metasodium antimonate has not proven injurious. However, he points out that the antimony oxide compounds (tartar emetic, etc.) are poisonous. For cast iron enamels, therefore, the use of $Na_2Sb_2O_3$ might be a perfectly feasible solution.

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